Cement chemistry

2nd edition

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Preface

The previous edition of this book, published by Academic Press in 1990, is both out of print and out of date, and when Thomas Telford invited me to prepare a new edition I was delighted to comply. I am most grateful both to them and to Academic Press, whose release of the copyright made the present edition possible.

This book deals with the chemistry of the principal silicate and aluminate cements used in building and civil engineering. It is directed primarily to those whose background is in chemistry, materials science or related disciplines. Emphasis is placed throughout on the underlying science rather than on practical applications, which are well covered in other works. The cements considered fall into the category of hydraulic cements; they set and harden as a result of chemical reactions with water, and if mixed with water in appropriate proportions continue to harden even if subsequently placed in water. Much the most important is Portland cement. Chapters 1 to 4 deal mainly with the chemistry of Portland cement manufacture and the nature of the resulting product. Chapters 5 to 8 deal mainly with the processes that occur when this product is mixed with water and with the nature of the hardened material. Chapters 9 to 11 deal with the chemistry of other types of cement, of admixtures for concrete and of special uses for cements. Chapter 12 deals with chemical and micro-structural aspects of concrete, including ones that affect its durability or limit its service life.

The literature of cement chemistry is voluminous; the abstracting journal, *Cements Research Progress*, has for some years listed around 1000 new contributions annually. The output of the seven years since the previous edition of this book appeared is reflected in the increased number of references to the literature, which is approximately 1500 compared with 1300 in that edition. Of necessity, coverage in the present book has been selective, but it is hoped that the most important contributions up to mid-1996 have been covered. The advances in some parts of the subject have been greater than in others, and this is reflected in the differences between this and the previous edition; some sections have been totally rewritten whereas others have changed relatively little.

As one who has seen the subject develop over a period of nearly 50 years, I am highly aware of the problems that those entering the subject

1 Portland cement and its major constituent phases

1.1 Introduction

1.1.1 Portland cement: general

Portland cement is made by heating a mixture of limestone and clay, or other materials of similar bulk composition and sufficient reactivity, ultimately to a temperature of about 1450°C. Partial fusion occurs, and nodules of clinker are produced. The clinker is mixed with a few per cent of calcium sulfate and finely ground, to make the cement. The calcium sulfate controls the rate of set and influences the rate of strength development. It is commonly described as gypsum, but this may be partly or wholly replaced by other forms of calcium sulfate. Some specifications allow the addition of other materials at the grinding stage. The clinker typically has a composition in the region of 67% CaO, 22% SiO_2, 5% Al_2O_3, 3% Fe_2O_3 and 3% other components, and normally contains four major phases, called alite, belite, aluminate and ferrite. Several other phases, such as alkali sulfates and calcium oxide, are normally present in minor amounts. Hardening results from reactions between the major phases and water.

Alite is the most important constituent of all normal Portland cement clinkers, of which it constitutes 50–70%. It is tricalcium silicate (Ca_3SiO_5) modified in composition and crystal structure by ionic substitutions. It reacts relatively quickly with water, and in normal Portland cements is the most important of the constituent phases for strength development; at ages up to 28 days, it is by far the most important.

Belite constitutes 15–30% of normal Portland cement clinkers. It is dicalcium silicate (Ca_2SiO_4) modified by ionic substitutions and normally present wholly or largely as the β polymorph. It reacts slowly with water, thus contributing little to the strength during the first 28 days, but substantially to the further increase in strength that occurs at later ages. By one year, the strengths obtainable from pure alite and pure belite are about the same under comparable conditions.

Aluminate constitutes 5–10% of most normal Portland cement clinkers. It is tricalcium aluminate ($Ca_3Al_2O_6$), substantially modified in composition and sometimes also in structure by ionic substitutions.

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It reacts rapidly with water, and can cause undesirably rapid setting unless a set-controlling agent, usually gypsum, is added.

Ferrite makes up 5–15% of normal Portland cement clinkers. It is tetra-calcium aluminoferrite (Ca_2AlFeO_5), substantially modified in composition by variation in Al/Fe ratio and ionic substitutions. The rate at which it reacts with water appears to be somewhat variable, perhaps due to differences in composition or other characteristics, but in general is high initially and low or very low at later ages.

1.1.2 Types of Portland cement

The great majority of Portland cements made throughout the world are designed for general constructional use. The standard specifications with which such cements must comply are similar, but not identical, in all countries and various names are used to define the material, such as Class 42.5 Portland cement in current European and British standards (42.5 is the minimum 28-day compressive strength in MPa), Types I and II Portland cement in the ASTM (American Society for Testing and Materials) specifications used in the USA, or Ordinary Portland Cement (OPC) in former British standards. Throughout this book, the term 'ordinary' Portland cements is used to distinguish such general-purpose cements from other types of Portland cement, which are made in smaller quantities for special purposes.

Standard specifications are, in general, based partly on chemical composition or physical properties such as specific surface area, and partly on performance tests, such as setting time or compressive strength developed under standard conditions. The content of MgO^* is usually limited to 4–5%, because quantities of this component in excess of about 2% can occur as periclase (magnesium oxide), which through slow reaction with water can cause destructive expansion of hardened concrete. Free lime (calcium oxide) can behave similarly. Excessive contents of SO_3 can also cause expansion, and upper limits, typically 3–5% for ordinary Portland cements, are usually imposed. Alkalis (K_2O and Na_2O) can undergo expansive reactions with certain aggregates, and some specifications limit the content, e.g. to 0.6% equivalent Na_2O ($Na_2O + 0.66 K_2O$). Other upper limits of composition widely used in specifications relate to matter insoluble in dilute acid, and loss on ignition. Many other minor components are limited in content by their effects on the manufacturing process, or the properties, or both, and in some cases the limits are defined in specifications.

Rapid-hardening Portland cements have been produced in various ways, such as varying the composition to increase the alite content, finer grinding of the clinker, and improvements in the manufacturing process,

*Confusion can arise because the names or formulae of compounds can be used to denote either phases or components; this applies especially to CaO and MgO. Here and elsewhere, chemical or mineral names of oxides (e.g. calcium oxide, magnesium oxide, lime, periclase) will generally be used for phases, and formulae (e.g. CaO, MgO) for components. Mineral names or prefixed formulae (e.g. α-Al_2O_3) are never used for components.

e.g. finer grinding or better mixing of the raw materials. The alite contents of Portland cements have increased steadily over the one and a half centuries during which the latter have been produced, and many cements that would be considered ordinary today would have been described as rapid hardening only a few decades ago. In the ASTM specifications, rapid-hardening Portland cements are called high early strength or Type III cements. For both ordinary and rapid-hardening cements, both lower and upper limits may be imposed on strengths at 28 days, upper limits being a safeguard against poor durability resulting from the use of inadequate cement contents in concrete.

Destructive expansion from reaction with sulfates can occur not only if the latter are present in excessive proportion in the cement, but also from attack on concrete by sulfate solutions. The reaction involves the Al_2O_3-containing phases in the hardened cement, and in sulfate-resisting Portland cements its effects are reduced by decreasing the proportion of the aluminate phase, sometimes to zero. This is achieved by decreasing the ratio of Al_2O_3 to Fe_2O_3 in the raw materials. In the USA, sulfate-resisting Portland cements are called Type V cements.

White Portland cements are made by increasing the ratio of Al_2O_3 to Fe_2O_3, and thus represent the opposite extreme in composition to sulfate-resisting Portland cements. The normal, dark colour of Portland cement is due to the ferrite, formation of which in a white cement must thus be avoided. It is impracticable to employ raw materials that are completely free from Fe_2O_3 and other components, such as Mn_2O_3, that contribute to the colour. The effects of these components are therefore usually minimized by producing the clinker under slightly reducing conditions and by rapid quenching. In addition to alite, belite and aluminate, some glass may be formed.

The reaction of Portland cement with water is exothermic, and while this can be an advantage under some conditions because it accelerates hardening, it is a disadvantage under others, such as in the construction of large dams or in the lining of oil wells, when a cement slurry has to be pumped over a large distance under pressure and sometimes at a high temperature. Slower heat evolution can be achieved by coarser grinding, and decreased total heat evolution by lowering the contents of alite and aluminate. The ASTM specifications include definitions of a Type II or 'moderate heat of hardening' cement, and a more extreme Type IV or 'low heat' cement. The Type II cement is also suitable for conditions exposed to moderate sulfate attack, and is widely used in general construction work. Heat evolution can also be decreased by partially replacing the cement by flyash (pulverized fuel ash; pfa) or other materials (Chapter 9), and this is today a widely used solution. The specialized requirements of oil well cements are discussed in Section 11.8.
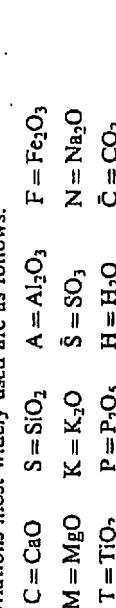
1.1.3 Cement chemical nomenclature and other abbreviations

Chemical formulae in cement chemistry are often expressed as sums of oxides; thus tricalcium silicate, Ca_3SiO_5, can be written as $3CaO \cdot SiO_2$. This does not imply that the constituent oxides have any separate

existence within the structure. It is usual to abbreviate the formulae of the commoner oxides to single letters, such as C for CaO or S for SiO_2, Ca_3SiO_5 thus becoming C_3S. This system is often combined with orthodox chemical notation within a chemical equation, e.g.

$$3CaO + SiO_2 \rightarrow C_3S \qquad (1.1)$$

or even within a single formula, as in $C_{11}A_7 \cdot CaF_2$ for $Ca_{12}Al_{14}O_{32}F_2$. The abbreviations most widely used are as follows.

$C = CaO$ $S = SiO_2$ $A = Al_2O_3$ $F = Fe_2O_3$

$M = MgO$ $K = K_2O$ $\bar{S} = SO_3$ $N = Na_2O$

$T = TiO_2$ $P = P_2O_5$ $H = H_2O$ $\bar{C} = CO_2$

The formulae of the simple oxide phases (e.g. CaO) are usually written in full. Other abbreviations and units used in this book are as follows.

1.1.3.1 Techniques

BEI = backscattered electron imaging. BSE = backscattered electron. DTA = differential thermal analysis. EPMA = electron probe microanalysis. ESCA = electron spectroscopy for chemical analysis (X-ray photoelectron spectroscopy). GLC = gas–liquid chromatography. GPC = gel permeation chromatography. IR = infrared. MIP = mercury intrusion porosimetry. NMR = nuclear magnetic resonance. QXDA = quantitative X-ray diffraction analysis. SEM = scanning electron microscop(e,y). STEM = scanning transmission electron microscop(e,y). TEM = transmission electron microscop(e,y). TG = thermogravimetry. TMS = trimethylsilyl(ation). XRD = X-ray diffraction. XRF = X-ray fluorescence.

1.1.3.2 Materials

C–S–H = poorly crystalline or amorphous calcium silicate hydrate of unspecified composition. Ggbs = ground granulated blastfurnace slag. Hcp = hardened cement paste. Pfa = pulverized fuel ash (flyash).

1.1.3.3 Properties or reactions

AR = alumina ratio (alumina modulus). ASR = alkali silica reaction. DEF = delayed ettringite formation. LSF = lime saturation factor. SR = silica ratio (silica modulus). C_x = analytical (total) concentration of x, irrespective of species. $[x]$ = concentration of species x. $\{x\}$ = activity of species x. RH = relative humidity. Na_2O_e = equivalent Na_2O (mass % $Na_2O + 0 \cdot 66\ K_2O$). $(+)2V$, $(-)2V$, optic sign and optic axial angle.

1.1.3.4 Pressure units

$1\ MPa = 1\ N\,mm^{-2} = 10\ bar = 9.87\ atm = 7500\ torr = 145 \cdot 0\ lb\,in^{-2} = 10 \cdot 198\ kg\,cm^{-2}$.

1.2 Alite

1.2.1 Polymorphism and crystal structure

On being heated, pure C_3S undergoes a series of reversible phase transitions, which have been detected by a combination of DTA,

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high-temperature XRD and high-temperature light microscopy (B1, G1, M1–M5, R1, R2, Y1):

$$T_1 \underset{620°C}{\rightleftharpoons} T_2 \underset{920°C}{\rightleftharpoons} T_3 \underset{980°C}{\rightleftharpoons} M_1 \underset{990°C}{\rightleftharpoons} M_2 \underset{1060°C}{\rightleftharpoons} M_3 \underset{1070°C}{\rightleftharpoons} R$$

(T = triclinic, M = monoclinic, R = rhombohedral)
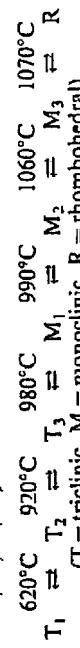
The pure compound, when cooled to room temperature, is thus T_1. In production clinkers, due to the incorporation of substituent ions, the form present at room temperature normally approximates to M_1 or M_3 or a mixture of these; rarely, T_2 is found (M1–M5,T1). There has been some uncertainty as to the number and nomenclature of these polymorphs; reported M_{1b} and M_{2b} forms appear to be identical with M_3, leaving reported M_{1a} and M_{2a} forms to be called simply M_1 and M_2 respectively (M4,M5).

Jeffery (J1) made the first determination of the crystal structure. He showed that the forms now known as R, T_1 and M_3 had closely similar structures, and determined the approximate or pseudostructure common to all three; it was built from Ca^{2+}, SiO_4^{4-} and O^{2-} ions, the last being bonded only to six Ca^{2+} ions, as in CaO. Later, more exact determinations were reported for T_1 (G2), M_3 stabilized by Mg^{2+} (N1), M_3 with increased disorder isolated from a works clinker (M6), R at 1200°C (N2) and R stabilized with Sr^{2+} (I1). Figure 1.1 shows the structure of the R form. The known structures are all closely similar as regards the positions of the Ca^{2+} and O^{2-} ions and of the Si atoms, but differ markedly in the orientations of the SiO_4^{4-} tetrahedra, which show varying degrees of disorder.

The structural differences between the polymorphs affect the coordination of the Ca^{2+} ions and the O atoms of the SiO_4^{4-} tetrahedra. For each polymorph, there are several crystallographically distinct Ca sites, having different coordination, and for a given site, the coordination sometimes varies between individual atoms due to orientational disorder in the surrounding SiO_4 tetrahedra. Definitions of the Ca coordination numbers are somewhat arbitrary due to variations in the lengths of the bonds; e.g. in the R form at 1200°C, the Ca atoms in one of the sites could be regarded as 7 coordinated if bonds as long as 0·296 nm are counted, and 5 coordinated if they are not (N2). If such abnormally long bonds are excluded, the mean coordination number of the Ca is 5·66 in the R polymorph, 6·15 in M_3 and 6·21 in T_1 (M5). In relation to reactivity towards water, the coordination of the oxygen atoms is possibly more important than that of Ca. This has not been discussed in detail in the literature, but mean oxygen coordination numbers may be expected to increase with those of calcium.

Table 1.1 gives the crystal data for the C_3S polymorphs that have been obtained using single-crystal methods. The literature contains additional unit-cell data, based only on powder diffraction evidence. Some of these may be equivalent to ones in Table 1.1, since the unit cell of a monoclinic or triclinic crystal can be defined in different ways, but some are certainly incorrect. Because only the stronger reflections are recorded, and for